

# **TOPIC 15 – ENERGETICS**

## **15.2: BORN–HABER CYCLE**

IB Chemistry

T15D10



# 15.2 Born-Haber Cycle

## - 2.5 hours

- 15.2.1 Define and apply the terms lattice enthalpy and electron affinity. (2)
- 15.2.2 Explain how the relative sizes and the charges of ions affect the lattice enthalpies of different ionic compounds. (3)
- 15.2.3 Construct a Born–Haber cycle for group 1 and 2 oxides and chlorides, and use it to calculate an enthalpy change. (3)
- 15.2.4 Discuss the difference between theoretical and experimental lattice enthalpy values of ionic compounds in terms of their covalent character. (3)



# 15.2.1 – Lattice Enthalpy and Electron Affinity

- 15.2.1 **Define** and **apply** the terms lattice enthalpy and electron affinity. (2)
- The **lattice enthalpy** ( $\Delta H^\theta_{\text{lattice}}$ ) of an ionic crystal is the heat energy absorbed (at const P) when one mole of a solid ionic compound is decomposed to form gaseous ions separated to an infinite distance from each other (under STP).
- The reverse would be heat energy released when one mole of ionic solid is formed from gaseous ions.



$$\Delta H^\theta_{\text{lattice}} = +701 \text{ —}$$

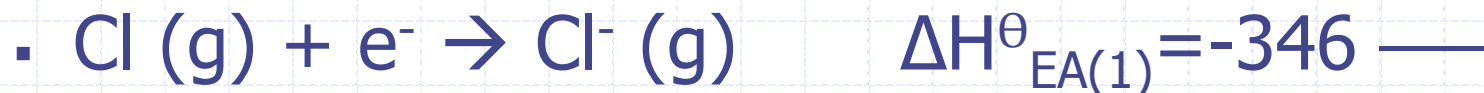
# 15.2.1 – Lattice Factors

- **Lattice energies** are a measure of the **stability** of a crystal.
- Greater values of lattice energy refer to a more energetically stable lattice which results in
  - Higher melting and boiling point
  - Effect on solubility (if soluble) of the salt
- The size of lattice energy is controlled by:
  - The charges on the ions
  - The ionic radii
  - Packing arrangement of the ions (type of lattice)



## 15.2.1 – Electron Affinity

- When an electron is acquired by an atom, energy is released, for example:



- The **first electron affinity**,  $\Delta H^\theta_{\text{EA}(1)}$ , is the energy released when one mole of gaseous atoms accepts one mole of electrons to form singly charged negative ions
- The **second electron affinity**,  $\Delta H^\theta_{\text{EA}(2)}$ , is the energy absorbed when one mole of gaseous ions with a single negative charge accept one mole of electrons, as in:



# 15.2.1 – Electron Affinity

- The second electron affinity,  $\Delta H^{\ominus}_{\text{EA}(2)}$ , is always endothermic because energy is required to overcome the mutual repulsion between the negatively charged  $\text{O}^-$  ion and the electron
- The first electron affinity,  $\Delta H^{\ominus}_{\text{EA}(1)}$ , usually correlates with electronegativity

Halogen	Electronegativity	$\Delta H^{\ominus}_{\text{EA}(1)}$ (—)
Fluorine	4.0	-348
Chlorine	3.0	-364
Bromine	2.8	-342
Iodine	2.5	-314



# 15.2.2 – Charge and Size effect on lattice enthalpies

- 15.2.2 **Explain** how the relative sizes and the charges of ions affect the lattice enthalpies of different ionic compounds. (3)
- For ionic compounds, the lattice energy depends on the attractive **electrostatic forces** operating between oppositely charged ions in the crystal
- Larger electrostatic forces of attraction result in larger lattice energies



## 15.2.2 – Lattice effects

- According to Coulomb's Law, the attractive force,  $F$ , operating between two adjacent oppositely charged ions in contact can be represented as follows:

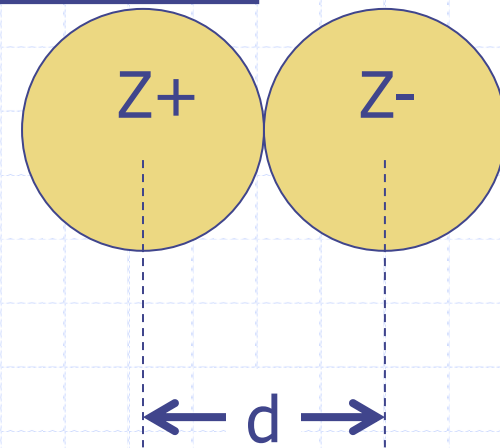
- $F \propto \frac{1}{d^2}$

- Ionic charge has huge impact

- $\Delta H^\theta_{\text{lattice}}[\text{MgO}] = +3889 \text{ kJ mol}^{-1}$

- $\Delta H^\theta_{\text{lattice}}[\text{NaF}] = +902 \text{ kJ mol}^{-1}$





- Lattice enthalpy for MgO is about 4x that of NaF
- This is largely due to the doubling charges of the ions as the sum of ionic radii and lattice structures are similar in both cases





## 15.2.2 – Lattice Effects

- The effect of **ionic radius** can be clearly seen in the sodium halides. The smaller the distance between the centers of the ions (sum of ionic radii), the larger the value of the lattice energy

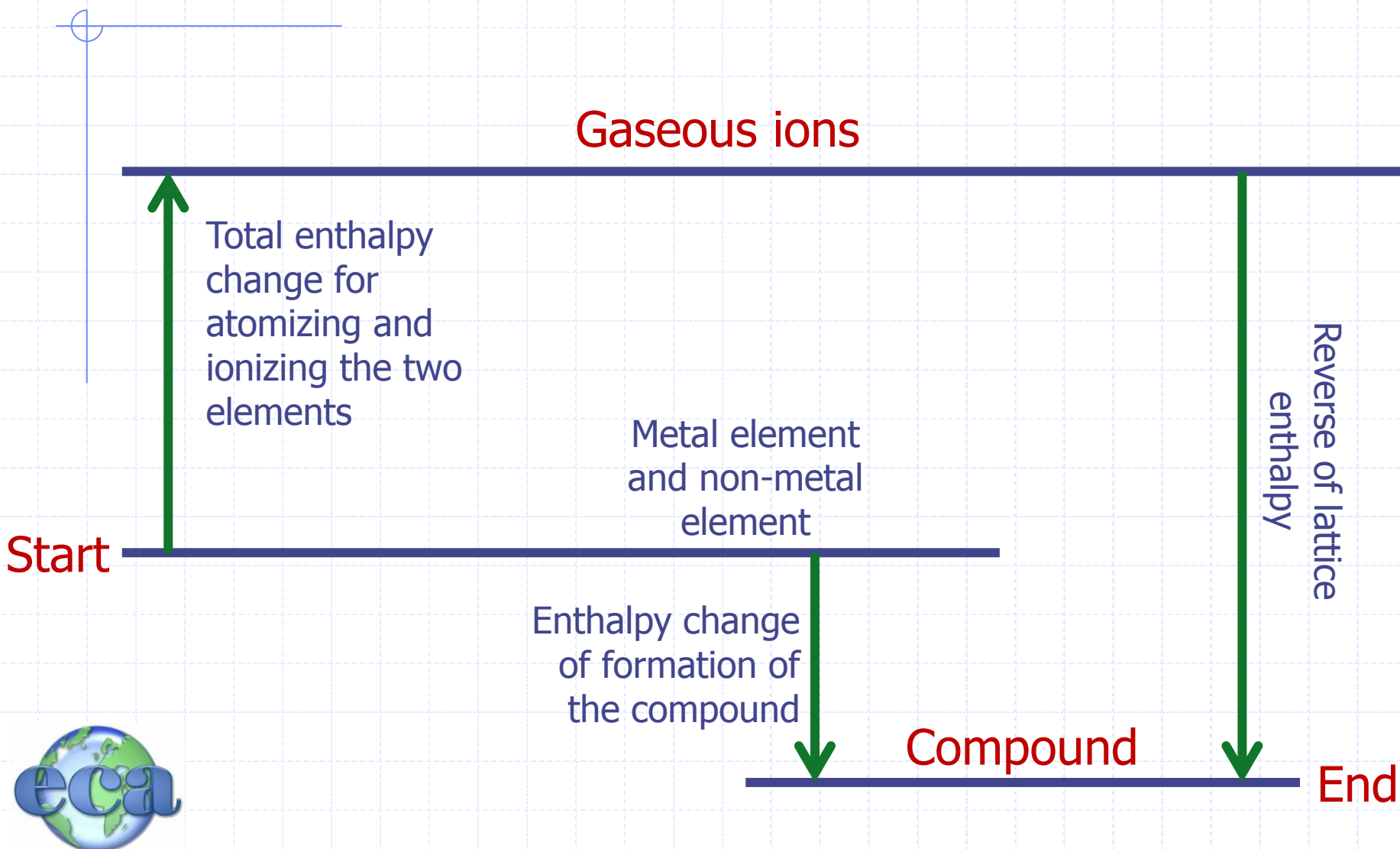
Sodium Halide	Radius of halide ion / nm	Distance between center of ions	Lattice enthalpy (—)
 Na <sup>+</sup> F <sup>-</sup>	0.133	0.231	+1902
 Na <sup>+</sup> Cl <sup>-</sup>	0.181	0.276	+771
 Na <sup>+</sup> Br <sup>-</sup>	0.196	0.291	+733
 Na <sup>+</sup> I <sup>-</sup>	0.219	0.311	+684

## 15.2.3 – Born-Haber Cycle

- 15.2.3 **Construct** a Born–Haber cycle for group 1 and 2 oxides and chlorides, and use it to **calculate** an enthalpy change. (3)
- Lattice enthalpies cannot be found directly from experiments (*partly because ionic crystals form ion pairs when heated, not free gaseous ions as needed*).
- Lattice enthalpies must be calculated indirectly from other known enthalpy changes of reaction using a **Born-Haber cycle**.



# 15.2.3 – Born-Haber Cycle



## 15.2.3 – Born-Haber

- Consider the reaction between sodium metal and chlorine gas to form sodium chloride
  - $\text{Na (s)} + \frac{1}{2} \text{Cl}_2 \text{ (g)} \rightarrow \text{NaCl (s)} \quad \Delta H^\theta_f = -411 \text{ —}$
- This reaction can be described also by the following equivalent pathway
  - $\text{Na (s)} \rightarrow \text{Na (g)} \quad \Delta H^\theta_{\text{at}} = +108 \text{ —}$
  - $\frac{1}{2} \text{Cl}_2 \text{ (g)} \rightarrow \text{Cl (g)} \quad \Delta H^\theta_{\text{at}} = +122 \text{ —}$
- Once these gaseous elements are formed, electron transfer can take place



$$\Delta H^\theta_{\text{IE}(1)} = +494 \text{ —}$$

First  
ionization  
energy



$$\Delta H^\theta_{\text{EA}(1)} = -364 \text{ —}$$

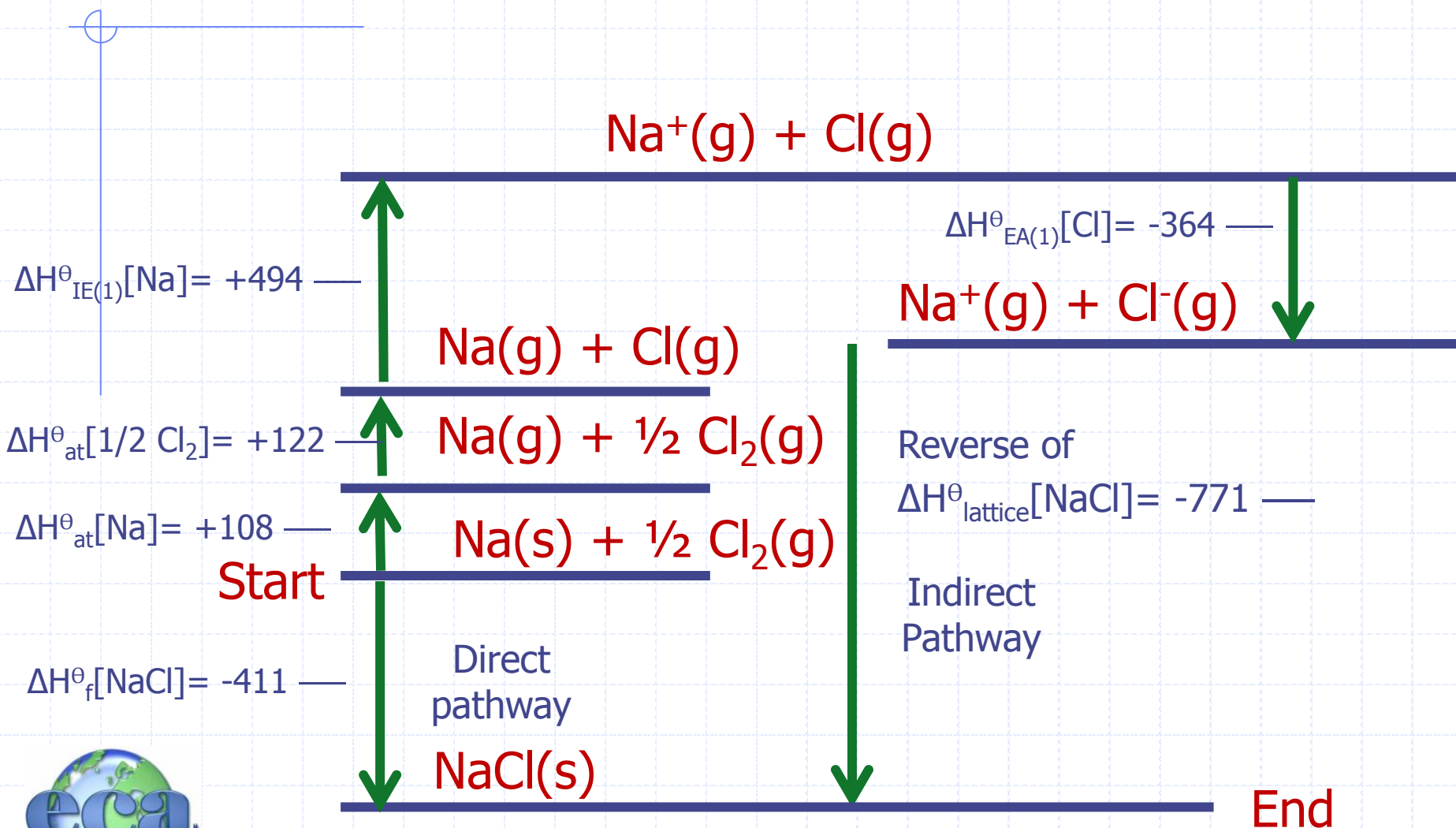
First  
electron  
affinity

## ....continued

- The oppositely charged ions exert powerful attractive electrostatic forces and form an ionic lattice of solid sodium chloride
  - $\text{Na}^+ (\text{g}) + \text{Cl}^- (\text{g}) \rightarrow \text{NaCl} (\text{s})$   $-\Delta H^\theta_{\text{lattice}} = -771 \text{ —}$
  - $\text{NaCl} (\text{s}) \rightarrow \text{Na}^+ (\text{g}) + \text{Cl}^- (\text{g})$   $\Delta H^\theta_{\text{lattice}} = +771 \text{ —}$
- When you take each step together the formation of sodium chloride from its elements can be summarized and the reverse lattice enthalpy calculated....



# 15.2.3 – Born-Haber NaCl



## 15.2.3 – Born-Haber Example

- Use the Born-Haber cycle to calculate the value of lattice enthalpy for Magnesium chloride
- Before we look at the chart, lets try to create it on our own!





$$2\Delta H^{\circ}_{\text{EA}(1)}[\text{Cl}] = 2 \times -364$$



$$\Delta H^{\circ}_{\text{IE}(1)}[\text{Mg}] = +736$$



Reverse of  
 $\Delta H^{\circ}_{\text{lattice}}[\text{MgCl}_2] = ?$

$$2\Delta H^{\circ}_{\text{at}}[1/2 \text{Cl}_2] = 2 \times +121$$



$$\Delta H^{\circ}_{\text{at}}[\text{Mg}] = +147$$



Indirect  
 Pathway

Start

$$\Delta H^{\circ}_{\text{f}}[\text{MgCl}_2] = -641$$

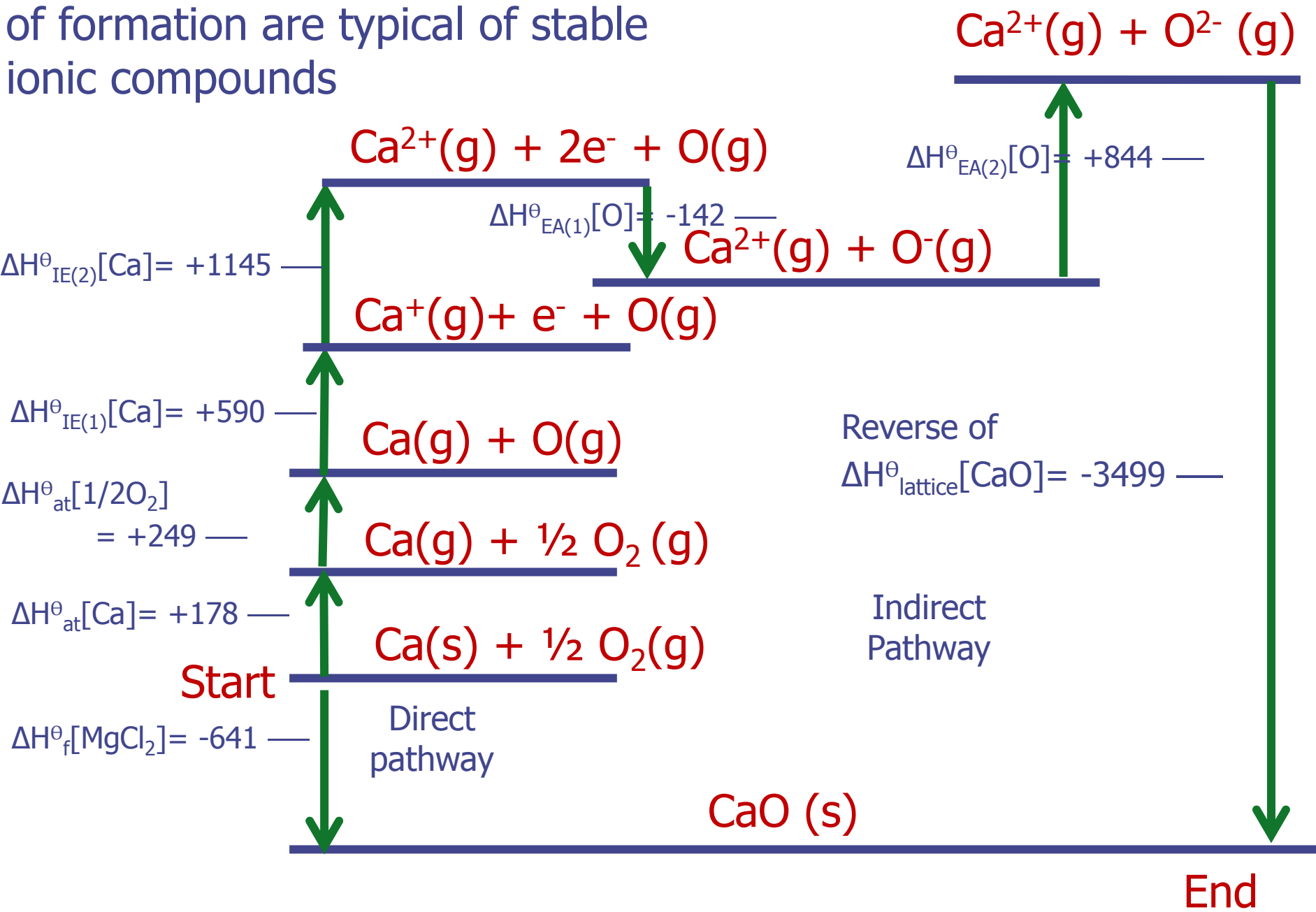
Direct  
 pathway



End



Large negative values of enthalpy of formation are typical of stable ionic compounds



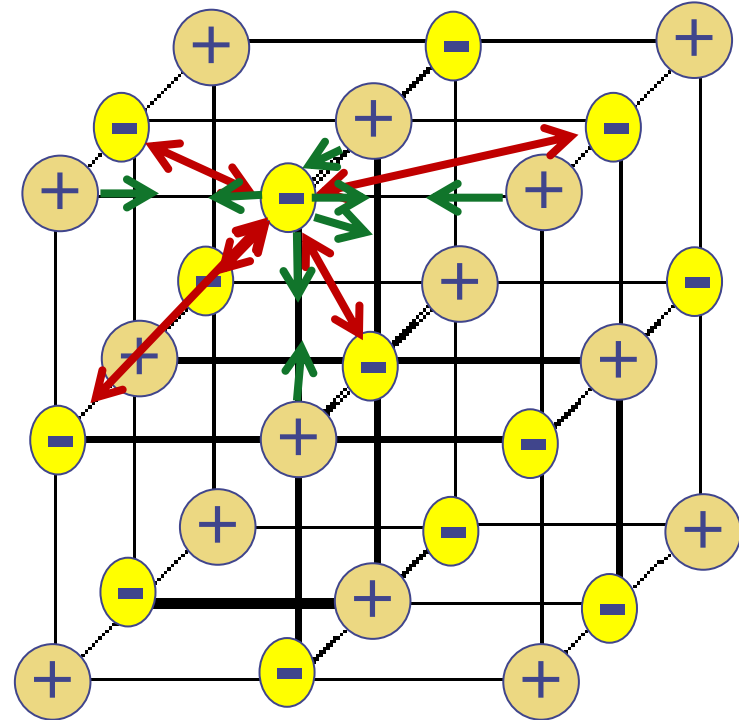
# 15.2.4 – Enthalpy difference based on Covalent character

- 15.2.4 Discuss the difference between theoretical and experimental lattice enthalpy values of ionic compounds in terms of their covalent character. (3)
- The lattice enthalpy can be found experimentally (indirectly) from the Born-Haber cycle.
- You can determine a theoretical value for comparison as well.
  - A simple model of an ionic bond is **two point charges** separated by an interionic distance. The potential energy between two ions changes as their distance changes.



## 15.2.4 – Exp vs. Theo

- The model can be extended to a three dimensional lattice including several atoms to give a theoretical value for the lattice enthalpy,  $\Delta H^{\theta}_{\text{lattice}}$
- There are both attractive and repulsive forces between the ions



# 15.2.4 – Theo v Exp Values

Compound	Theoretical Lattice enthalpy —	Experimental Value (from B-H) —	Percentage Difference
NaCl	766	771	0.06
NaBr	732	733	0.01
NaI	686	684	0.29
KCl	690	701	0.15
KBr	665	670	0.75
KI	632	629	0.48
AgCl	770	905	14.9
AgBr	758	890	14.8
AgI	736	876	16.0



# 15.2.4 – Alkali Metal Halide Models

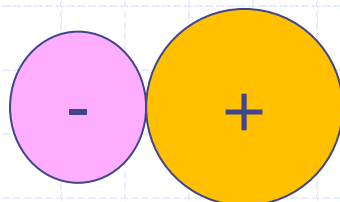
- For alkali metals (Na, K, etc) there is very good agreement between the theoretical and experimental values derived from the B-H cycle.
  - Therefore, a purely ionic model is therefore a good description of the bonding within the alkali metal halides
  - This is due to the large electronegativity difference and hence there is almost a complete electron transfer and little electron density between ions (little or no covalent sharing)



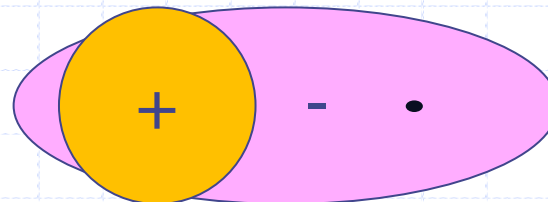
## 15.2.4 – Silver Halide Models

- The silver halides are a different story as there is poor agreement between the two values.
  - The bonding of the silver halides is stronger than the predicted by a purely ionic model.
  - The bonding is not purely ionic because of incomplete transfer of valence electrons between atoms. This results in electron density between cation and anion (covalent sharing)


ion pair



covalent sharing



## 15.2.4 – Ionic Solids in Water

- The ionic character of the compound begins to explain the thermodynamic properties (endo vs exo) for the dissolving of ionic solids in water.
    - Lattice enthalpies are always endothermic
    - Ion-dipole bond formation is exothermic
      - Hydration is always exothermic
    - The difference in the two make the process endo- or exo-thermic
    - $\Delta H^{\theta}_{\text{sol}}$ , enthalpy change of solution
    - $\Delta H^{\theta}_{\text{hyd}}$ , enthalpy change of hydration
-  Hess's Law cycle can be used to represent the cycle of ionic solids dissolving in water